Preparation of Novel Monomers for Rigid-Rod Polymers

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ABSTRACT

PREPARATION OF NOVEL MONOMERS FOR RIGID-ROD POLYMERS

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The initial focus of the project was the synthesis and processing of rigid-rod polymers that are sufficiently compatible to be homogeneously dispersed on the molecular scale, leading to a molecular-level or angstrom-scale composite (ÅSC). The outcomes from several attempts to prepare the ÅSC were not consistent in terms of polymer chain length and polymer solubility. This was partially attributed to a loss of sulfonic acid functional groups, at the employed temperature conditions. Consequently, the focus was on the preparation and employment of modified acidic group-containing monomers, less prone to undergo defunctionalization upon temperature increase.

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LIST OF SYMBOLS/ABBREVIATIONS

^1H: Proton

ÅSC: Angstrom-scale composite

Bu_4NBr: Tetrabutlyammoniumbromide

$CDCl_3$: Deuterated chloroform

CH_2Cl_2: Methylene chloride

CH_3CN: Acetonitrile

CO_2: Carbon dioxide

D_2O: Deuterium oxide

DME: Dimethoxyethane

DMF: Dimethylformamide

DMSO: Dimethylsulfoxide

EDC: 1,2-Dichloroethane

Et_3N^+H: Triethylammonium cation

H_2O: Water

H_2SO_4: Sulfuric acid

HCl: Hydrochloric acid

$KMnO_4$: Potassium permanganate

MSA: Methanesulfonic acid

$MgSO_4$: Magnesium sulfate

Na_2SO_3: Sodium sulfite

$Na_2S_2O_8$: Sodium persulfate

NBS: N-bromosuccinimide

n-BuLi: *N*-Butyllithium

NH_3: Ammonia

$NiCl_2$: Nickel chloride

NMP: *N*-Methyl-2-pyrrolidinone

NMR: Nuclear magnetic resonance

PANI: Polyaniline

PBO: Poly(*p*-phenylenebenzobisoxazole)

$PdCl_2$: Palladium chloride

$PO_3ClC_4H_{10}$: Diethylchlorophosphate

$POCl_3$: Phosphorus oxychloride

PPA: Polyphosphoric acid

PPBI: Phosphonic acid pendant poly(*p*-phenylenebenzobisimidazole)

PBZT: Poly(*p*-phenylenebenzobisthiazole)

SMPBI: Sulfomethyl pendant poly(*p*-phenylenebenzobisimidazole)

S_NAr: Nucleophilic aromatic substitution

SPBI: Sulfonic acid pendant poly(*p*-phenylenebenzobisimidazole)

t-BuLi: *t*-Butyllithium

THF: Tetrahydrofuran

TLC: Thin layer chromatography

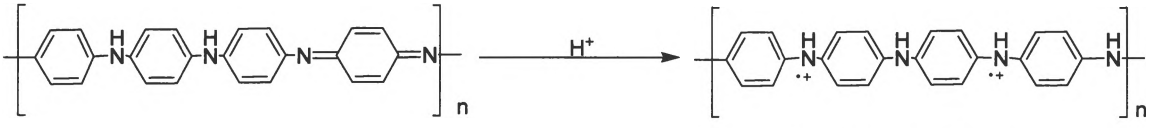
CHAPTER 1

INTRODUCTION

Electrically conductive polymers have potential for a wide variety of military and civilian applications including paints and coatings, antistatic formulations, electromagnetic shielding, and electronic devices.[1] Polyaniline (PANI) is the most promising and widely investigated of the conducting polymers and is commercially available.[2,3] In order to become a useful conducting material, PANI must be converted from its insulating emeraldine base to a conducting emeraldine salt form by a protonic dopant such as a strong acid, Figure 1.[4]

Figure 1

Structure of protonated PANI



Emeraldine Base (Insulating) Emeraldine Salt (Conducting)

Although early efforts to process PANI into useful forms were hampered by its intractable and infusible nature, great strides have been made in recent years in improving the processibility of PANI. A major breakthrough has been the use of organic sulfonic acids such as camphor sulfonic acid and *p*-dodecylbenzensulfonic acid as protonic

dopants that impart high conductivity as well as fusibility and solubility of PANI in selected organic solvents.[5,6] This has led to studies of conducting blends of PANI with a wide range of commercially available thermoplastics.[5,7-9] Blends were formulated, in part, because of the relatively fragile nature of PANI films and fibers, primarily attributable to the limited molecular weight of PANI. Acceptable electrical conductivities and mechanical properties were recorded for these blends; however, potential applications were limited because of their modest thermal stabilities.

An alternative method for processing PANI in its protonated state was pursued by Tan *et al.* and involved casting blended films from solutions of PANI and poly(*p*-phenylenebenzobisthiazole) (PBZT) in methanesulfonic acid.[10] PBZT belongs to a class of lyotropic rigid-rod polymers that can be fabricated from nematic solutions into highly oriented fibers and films that exhibit exceptional tensile strength and modulus in addition to outstanding environmental stability.[11] In this process, methanesulfonic acid served as both a protonic dopant for PANI and a solvent for the polymers, thus eliminating the need for a subsequent protonation step following fabrication. The PANI/thermoplastic films were non-homogeneous because of the thermodynamically driven phase separation of PBZT and PANI. Morphological studies demonstrated a phase-separation system at the micrometer-to-nanometer level with conductivity being achieved through a continuous PANI network. Similar continuous PANI networks were also observed earlier for PANI/poly(*p*-phenylene terephthalamide) (Kevlar) blends.[12,13] This phase separation and lack of polymer chain orientation limited the electrical and mechanical properties of the blend.

In order to more fully realize the potential of PANI as a mechanically and

thermally robust, electrically conducting polymer, research is needed to achieve highly oriented (anisotropic) and completely homogeneous blends of protonically-doped PANI with a robust rigid-rod polymer such as PBZT. Orientation and maximum extension of the PANI polymer chain will optimize its inherent conductivity, while the fully conjugated backbone of PBZT or related polymer should provide an efficient conductive pathway for the global mobility of the charge carriers. This approach to obtaining a mechanically and thermally robust conducting polymer is expected to be most feasible if the blend is homogenous at the molecular level.

This idea is referred to as a "rigid-rod molecular scaffold", or an "angstrom-scale composite" (ÅSC). It is a true composite in the sense that two or more components combine in a synergistic manner. In the proposed case, the maximum electrical conductivity of PANI is achieved by stretching out the inherently conductive polymer chains on a rigid-rod polymer that serves as a "scaffolding." In addition to this function, the scaffolding serves as a mechanically and thermally stable structure that will translate to attractive bulk thermo-mechanical properties. This concept is different from conventional composites and nanocomposites in that the dispersion of the components is on the molecular level, which is expected to lead to far-reaching implications.

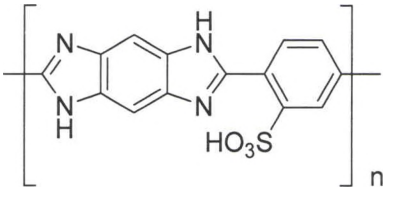
In the ÅSC concept, the scale of interaction of the material constituents is reduced from the nanometer level to the "basement" of material science, i.e. the molecular level. Like in nanotechnology, one of the known fundamental advantages of reducing the scale of material constituents is the reduction in material defects, which leads to improved properties. In addition, many unexpected phenomena arise that researchers are only beginning to observe and understand. These unexpected phenomena are expected to play

a key role in designing new materials with tailored, multifunctional properties. Traditionally, material properties must be balanced by sacrificing one property to increase another. With nano- and molecular-level materials, several properties can be optimized simultaneously. It is possible that ÅSCs will even outpace nanomaterials in this respect. In the current project, the ÅSCs were expected to exhibit both high temperature mechanical robustness as well as electrical conductivity. This combination of properties would have enormous impact on many defense-related applications (conducting coatings, plastic wires) as well as commercial, industrial, and transportation applications (fuel cells).

For this to be achieved, an approach must be formulated to defeat the thermodynamically driven phase separation of PANI and the rigid-rod polymer. In an attempt to achieve a truly homogenous polymeric blend at the molecular level and concomitant improvement of mechanical and electrical properties, we proposed the preparation of thermally stable and mechanically robust conductive films or fibers from blends of PANI and a sulfonic acid pendant poly(*p*-phenylenebenzobisimidazole), SPBI (Figure 2).[14]

Figure 2

Structure of SPBI



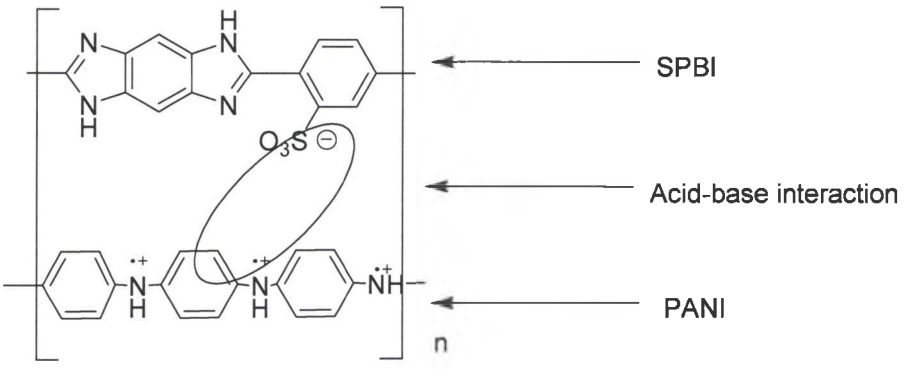
Sulfonic acid pendant poly(*p*-phenylenebenzobisimidazole)

SPBI is a functionalized member of the family of environmentally stable rigid-rod polymers that include PBZT and commercially available poly(*p*-phenylene benzobisoxazole), (PBO).[11] SPBI would be expected to impart a high degree of environmental stability and exceptional mechanical properties to the ÅSC, while the PANI would provide the "circuit" for electrical conductivity.

The key step in this approach to achieve a truly homogenous molecular blend entails acid-base interaction of the pendant sulfonic acid groups in SPBI with the basic secondary amine groups in the polyaniline (PANI) backbone as shown in Figure 3.

Figure 3

Angstrom-Scale Composite (ÅSC)



This interaction will serve several purposes: 1) It will convert PANI from the insulating emeraldine base form to the conductive emeraldine salt form. Furthermore, the SPBI polymer chains would serve in the capacity as an extremely immobile and stable "dopant", possibly obviating the loss of conductivity observed in other PANI/dopant systems. 2) This same strong ionic interaction will serve as a stable tie between the SPBI and PANI polymer chains at the molecular level, ensuring a truly homogeneous blend and extremely uniform electrical and mechanical properties in the resultant films or

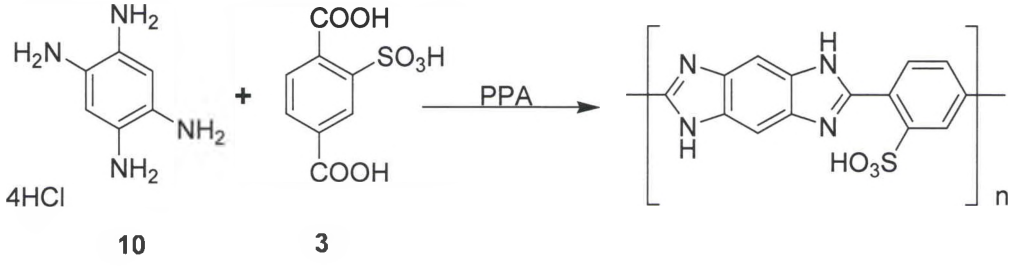
fibers.

The basic ÅSC concept *via* acid-base interaction has been demonstrated through recent ground-breaking work by Dang *et al.*, with the exception that other (nonconductive) compounds were used instead of PANI.[15,16] Films cast from SPBI and thermoplastic and thermoset polymers containing basic amine groups were shown by detailed morphology studies to be highly miscible with no observable phase-separated domains. Based on the success of those studies, we can reasonably expect that the proposed PANI/SPBI films or fibers will also be homogeneous at the molecular level, thus leading to beneficial mechanical and electrical properties.

The research initially centered on obtaining the requisite monomers for PANI and SPBI. Although aniline (i.e. the monomer for PANI) is readily available, the monomers for SPBI had to be synthesized. SPBI is readily prepared as a lyotropic solution by the co-polycondensation of 1,2,4,5-tetraaminobenzene tetrahydrochloride with 2-sulfoterephthalic acid in polyphosphoric acid (PPA), (Figure 4).[16]

Figure 4

Preparation of SPBI



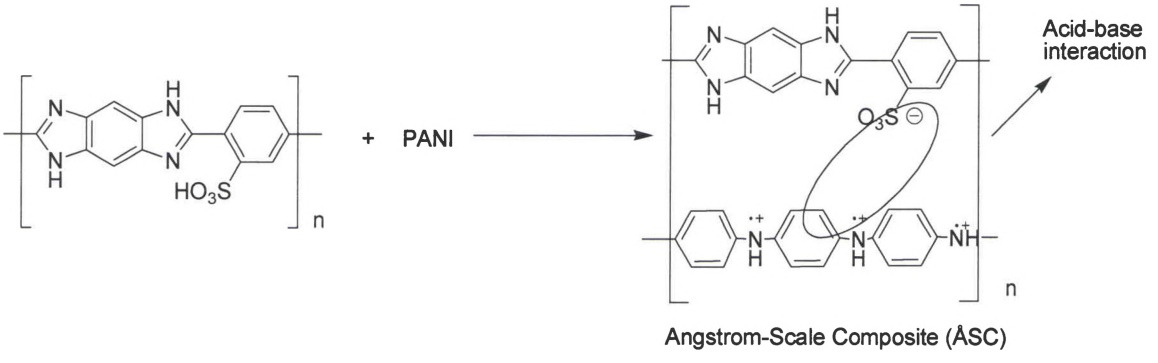
In order to produce cast films, it is necessary to prepare solutions of PANI and SPBI in solvents amenable to standard film casting techniques. Rigid-rod polymers are ordinarily

soluble only in strong acids such as methanesulfonic acid and the resultant solutions are not readily amenable to film casting. However, earlier studies have demonstrated that SPBI can be more conveniently solubilized as its triethylammonium (Et_3N^+H) salt in selected organic solvents.[16] In this study, solubilization was achieved by conversion to Et_3N^+H salt in N-methyl-2-pyrrolidinone (NMP). Isotropic films could then be cast from a solution of the PANI/SPBI blend using standard casting techniques.

PANI is solubilized in a lyotropic solution of SPBI in polyphosphoric acid (PPA) to give a lyotropic dope suitable for extrusion and coagulation into anisotropic fibers and films. Although simple in principle, formation of the requisite lyotropic dope is hindered by the high bulk viscosities of the lyotropic solutions. Previous investigations have demonstrated the formation of highly anisotropic fibers and films of rigid-rod polymers *via* an extrusion/coagulation process. [11] In the present case, SPBI can form a lyotropic nematic phase and serve as a scaffold for the PANI polymer chains during extrusion and coagulation. The resultant high chain extension is expected to contribute to maximization of the PANI electrical conductivity (Figure 5).

Figure 5

Preparation of ÅSC

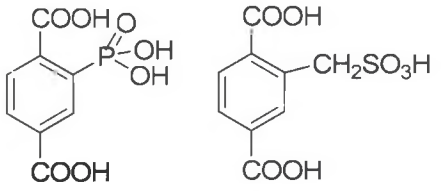


Although initial efforts were focused on the preparation of the 1,2,4,5-tetraaminobenzene (**9**) and 2-sulfoterephthalic acid (**3**), the use of 2-sulfoterephthalic acid turned out to be incompatible with the generation of rigid-rod polymer with the desired qualities, particularly higher chain-length. The outcomes from several attempts were not consistent, in terms of polymer chain length and polymer solubility. It was found out that, in general, exposure of the polymerization mixtures to higher reaction temperatures led to samples with reduced solubility, at least partially attributable to certain degree of loss of sulfonic acid functional groups, at the employed temperature conditions. It became obvious that the production of polymer with satisfactory chain length, which is promoted by elevated temperatures, is accompanied by loss of sulfonic acid functional groups and thereby of solubility. Consequently, we focused our attention on the preparation and employment of modified acidic group-containing monomers, less prone to undergo defunctionalization upon temperature increase.

The current report details our efforts towards the preparation and characterization of two particular structures: 2-phosphonoterephthalic acid, **13**, and 2-(sulfomethyl) terephthalic acid, **23** (Figure 6). 2-Phosphonoterephthalic acid has been previously reported in two patent sources,[17,18] while 2-(sulfomethyl)terephthalic acid is a new compound, whose synthesis and characterization we report for the first time. For various reasons, stated in the next section, we found it necessary to develop a new synthetic protocol for the preparation of 2-phosphonoterephthalic acid.

Figure 6

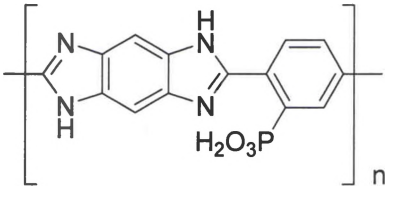
Structures of 2-phosphonoterephthalic acid and 2-(sulfomethyl)terephthalic acid



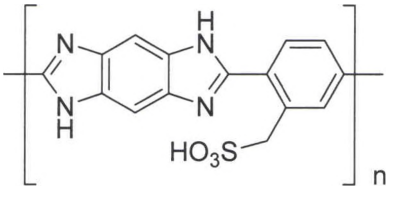
2-Phosphonoterephthalic acid or 2-(sulfomethyl)terephthalic acid can replace 2-sulfoterephthalic acid in the co-polycondensation reaction to form either phosphonic acid pendant poly(*p*-phenylenebenzobisimidazole) (PPBI) or sulfomethyl pendant poly(*p*-phenylenebenzobisimidazole) (SMPBI) as seen in Figure 7. The production of cast films will proceed as done with SBPI/PANI.

Figure 7

Structure of PPBI and SMPBI



Phosphonic acid pendant poly
(*p*-phenylenebenzobismidazole)



Sulfomethyl acid pendant poly
(*p*-phenylenebenzobismidazole)

CHAPTER 2

RESULTS AND DISCUSSION

Part I: Preparation of 2-sulfoterephthalic acid and 1,2,4,5-tetraaminobenzene

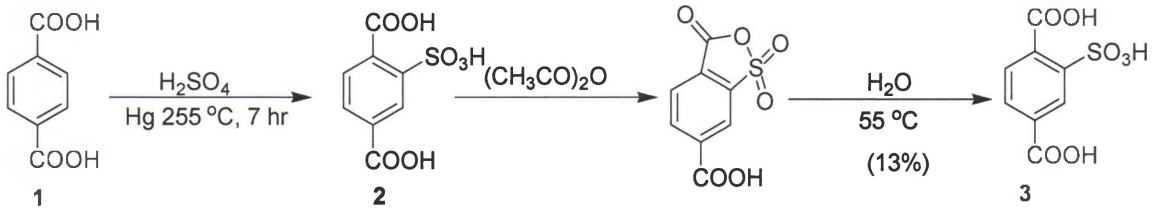
Preparation of 2-sulfoterephthalic acid

Substituted terephthalic acids, with pendant acidic functional group, have found numerous applications. The best-known example among them is 2-sulfoterephthalic acid, which has been employed extensively in the preparation of various materials, among them polybenzobis(imidazole) and polybenzobis(thiazole) rigid-rod polymers[14], polyesters for laundry detergent additives and friction-reducing agents, ink-drying agents for ink-jet printers, dopants for electrically-conductive polymers such as polypyrrole and polythiophenes.[19]

In the past, 2-sulfoterphthatlic acid has been produced using terephthalic acid as the starting material, as shown in Scheme 1.[20] Terephthalic acid, on sulfonation with fuming sulfuric acid in the presence of a catalytic amount of mercury gives, crude 2-sulfoterephthalic acid. This material is partially purified by dissolving it in water and precipitating it out by saturating the solution with HCl-gas. It is further purified by recrystallization from glacial acetic acid. The final purification is achieved by converting the acid into the corresponding anhydride followed by hydrolysis.[20]

Scheme 1

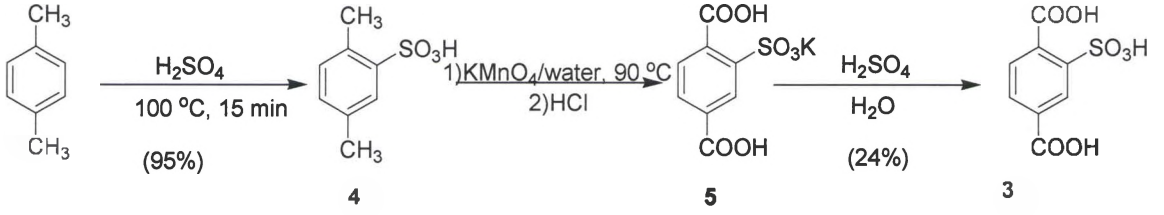
Literature method for preparation of 2-sulfoterephthalic acid



Due to the low yield and extreme conditions, we endeavored to design a new method. The procedure, shown in Scheme 2, employs *p*-xylene as the starting material. Since *p*-xylene is an activated benzene ring, sulfonation of the ring readily occurs through an electrophilic aromatic substitution with 98% H_2SO_4, resulting in 2,5-dimethylbenzenesulfonic acid (**4**). 2,5-Dimethlybenzenesulfonic acid (**4**) is oxidized using potassium permanganate in water, at 90 °C, followed by acidification. The resultant potassium 2,5-dicarboxybenzenesulfonate (**5**) is easily purified *via* recrystallization from water.[21]

Scheme 2

Improved synthesis of 2-sulfoterephthalic acid



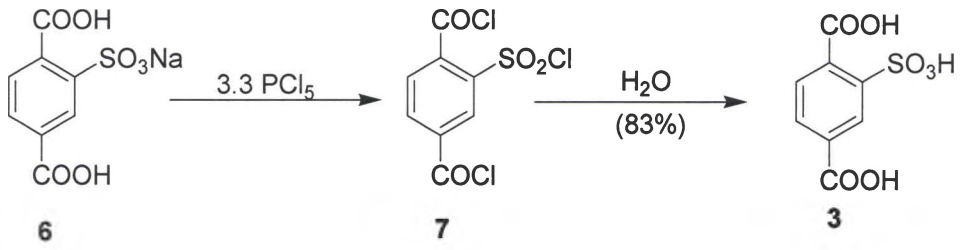
The major challenge of this procedure is the conversion of the K-salt to the free acid (**3**). After several unsuccessful attempts, it was discovered that submitting **5** to several sequential treatments with concentrated sulfuric acid/water yields the free acid.

Purification of the acid was done *via* recrystallization from concentrated hydrochloric acid.

The conversion of salt to free acid was further improved as shown in Scheme 3. Sodium or potassium 2,5-dicarboxybenzenesulfonate is reacted with 3.3 equivalents of phosphorus pentachloride (PCl_5) to form the trichloride, **7.** With no further purification **7** is subjected to hydrolysis to form the free acid, **3**. The acid is submitted to extensive drying under high vacuum.

Scheme 3

Current synthesis of 2-sulfoterephthalic acid

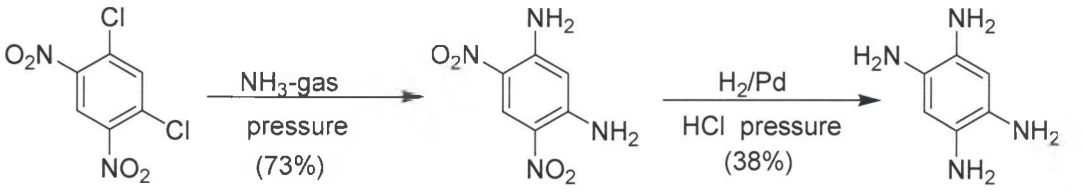


Preparation of 1,2,4,5-tetraaminobenzene

The other required monomer in the synthesis of SPBI is 1,2,4,5-tetraaminobenzene. Its synthesis, as reported in literature (Scheme 4), starts with 1,5-dinitro-2,4-dichlorobenzene.[20] It reacts with anhydrous ammonia at 150 - 170 °C in a Hastelloy-C autoclave to furnish the diamino compound. The product is recrystalized from dioxane and dimethylformamide (DMF). Catalytic reduction of the purified 4,6-dinitrobenzene-1,3-diamine (**8**) at 100 psi of hydrogen in 10% hydrochloric acid gives the desired 1,2,4,5-tetraaminobenzene (**9**).[20] Overall, the yield is 28% and the process requires harsh conditions.

Scheme 4

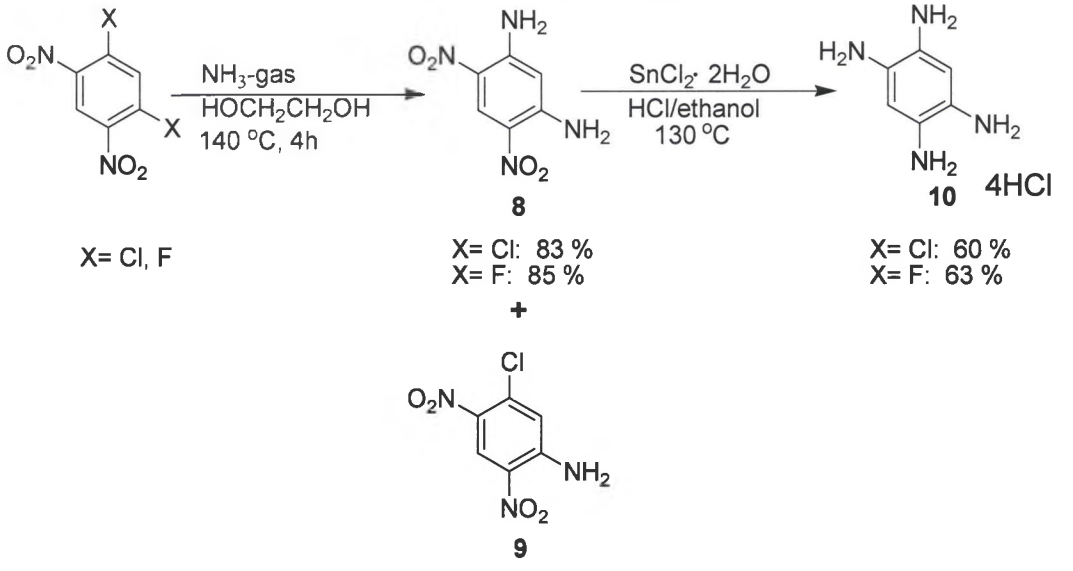
Previous method for formation of 1,2,4,5-tetraaminobenzene



In an attempt to design and implement an improved procedure, we managed to avoid conditions such as high pressure, at the same time increasing the yield The new procedure (Scheme 5) begins with 1,5-dinitro-2,4-dichlorobenzene, which is reacted with ammonia gas in ethylene glycol and undergoes a nulceophilic aromatic substitution to form 2,5-dinitrobenzene-1,3-diamine (**8**).[22] The product is then recrystallized from dioxane and DMF to insure no impurities are present. Through reaction of **8** with $SnCl_2$ the nitro groups are reduced, to form **9**, which was recrystallized from conc. HCl/water.[23]

Scheme 5

Improved synthesis of 1,2,4,5-tetraaminobenzene



An even more efficient procedure, recently implemented, begins with 1,5-dinitro-2,4-difluorobenzene (Scheme 5) instead of 1,5-dinitro-2,4-dichlorobenzene. Since fluorine is more electronegative than chlorine, it is a better leaving group in S_NAr reactions, leading to higher yields and cleaner products. The use of 1,5-dinitro-2,4-difluorobenzene is therefore recommended, in place of 1,5-dinitro-2,4-dichlorobenzene, in the preparation of 1,2,4,5-tetraaminobenzene.

The major challenge in producing **10** is the purity of the final product. 1,2,4,5-Tetraaminobenzene, **10**, is too sensitive to be subjected to a lengthy purification, so the intermediate **8** is the final stage to conduct purification before the polymerization. 2,5-Dinitrobenzene-1,3-diamine, **8**, is formed along with 5-chloro-2,4-dinitroaniline, **9**, a byproduct. Compound **8** was recrystalized three times from DMF and 1,4-dioaxane to ensure the purity of the compound. Also, TLC and HPLC were performed to confirm

that only 2,5-dinitro-1,3-diamine was present.

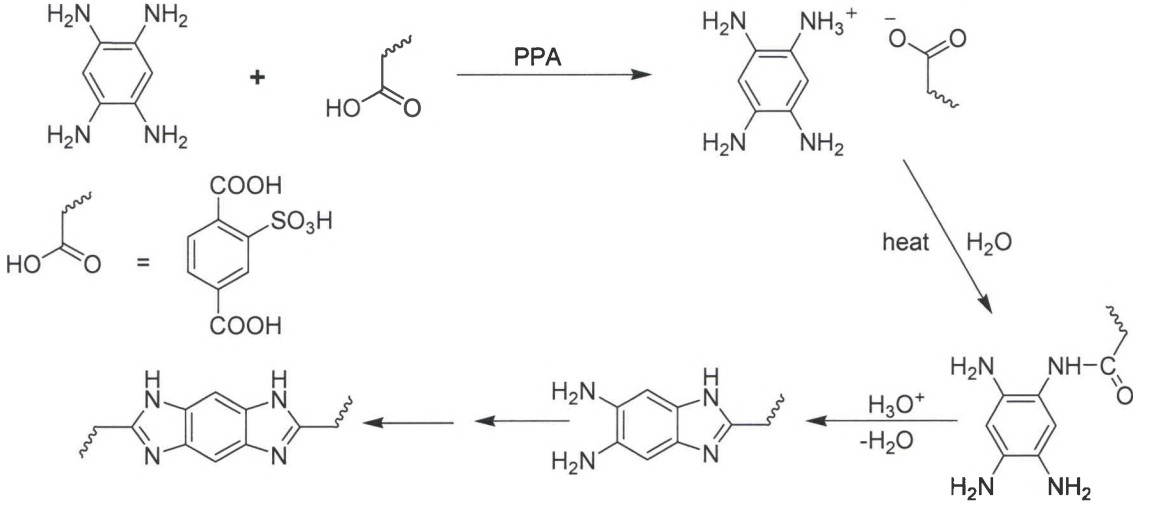
Part II: Polymerization reactions and attempts to prepare an ÅSC composite

Preparation of SPBI

SPBI is prepared as a lyotropic solution by the co-polycondensation of 1,2,4,5-tetraaminobenzene with 2-sulfoterephthalic acid in polyphosphoric acid (PPA) (Scheme 6). The mixture is degassed and HCl is removed by the use of a vacuum and a lead acetate bubbler. Two different polymerizations were done initially, each with a different cure process. The temperature was monitored closely to ensure that a high molecular weight material was obtained while maintaining the solubility of the polymer. All SBPI samples were freeze-dried in order to get high surface area, which would help increase the solubility of the polymer.

Scheme 6

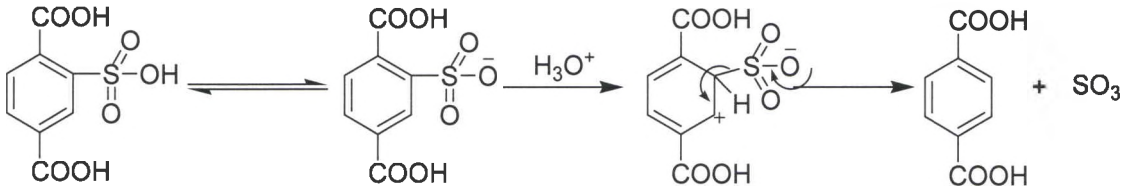
Mechanism of SPBI



Both SPBI samples obtained were insoluble in a variety of different solvents. We attribute this to de-sulfonation of the polymer at elevated temperatures (Scheme 7).

Scheme 7

De-sulfonation of SPBI



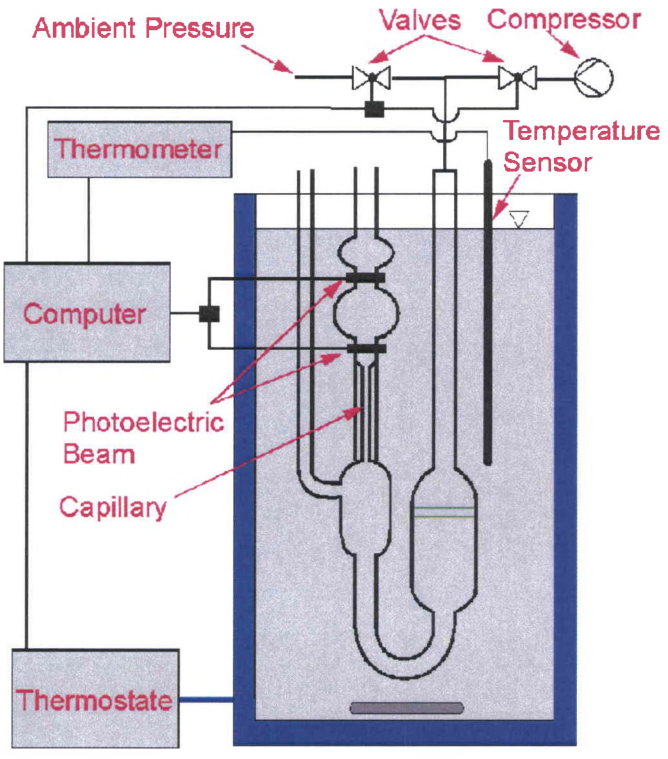
Therefore, new acidic monomers were developed, which are expected to retain their acidic functionality at elevated temperatures.

Intrinsic Viscosity Measurements

Polymer scientists are normally interested in the variation of the solution viscosity with molar mass. Unfortunately no theories have been developed to relate them to each other and empirical relationships are used to determine the molar mass of a polymer sample from measurements of solution viscosity. However, this method does have the distinct advantage of being a rapid technique that can be carried out quickly using relatively simple apparatus.[24] The most useful kind of viscometer for determining intrinsic viscosity is the "suspended lever" or Ubbelohde viscometer (Figure 8).

Figure 8

Ubbelohde Viscometer



The viscometer is called "suspended level" because the liquid initially drawn into the small upper bulb is not connected to the reservoir as it flows down the capillary during measurement. The capillary is suspended above the reservoir. In conjunction with the pressure-equalization tube, this ensures that the only pressure difference between the top of the bulb and the bottom of the capillary is that due to the hydrostatic pressure--i.e., the weight of the liquid.[25] The rate of flow of liquid through a capillary of radius r and length l is given by Poiseuille's equation as

$$\frac{dV}{dt} = \frac{\pi p r^4}{8\eta l} \qquad (1)$$

where η is the viscosity of the liquid, p the pressure head causing the flow and dV/dt is the volume of the liquid flowing through the capillary in unit time. The pressure head, p, continually decrease during an experiment and so it is convenient to define an average pressure $\bar{p}$. A constant volume of liquid V is normally used and so Equation 1 can be approximated to

$$\frac{V}{t} = \frac{\pi \bar{p} r^4}{8\eta l} \tag{2}$$

where t is the time of flow the liquid through the capillary.[24] We are normally interested in the difference between the flow times of the solution and pure solvent and so if the subscript $_o$ is used to designate the solvent then Equation 2 can be written as[24]

$$\frac{V}{t} = \frac{\pi \bar{p} r^4}{8\eta l} \rightarrow solution$$

$$\frac{V}{t} = \frac{\pi \bar{p}_0 r^4}{8\eta_0 l} \rightarrow solvent$$

where η is the viscosity of the solution and η_0 is that of the pure solvent. The average pressure producing flow is given by the standard relation

$$\bar{p} = \rho g \bar{h} \tag{3}$$

where ρ is the density of the liquid, $\bar{h}$ the average head of liquid and g the acceleration due to gravity.[24] Equation 3 can clearly be used to determine the viscosity η of a polymer solution if the viscometer is calibrated with liquids of known viscosity. However, we are not normally interested in the absolute viscosity of the solution, but are more concerned with the increase in viscosity of the solvent caused by the presence of the polymer

molecules. A parameter of considerable importance is the *viscosity ratio* or *relative viscosity*, η_r, which is define as (η/η_0) and can be related to the flow times t and t_0 through Equations 2 and 3 which lead to

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t\rho}{t_0\rho_0} \tag{4}$$

This equation can be further simplified since for a dilute solution $\rho \approx \rho_0$ and so η_r is normally taken as t/t_0. Since η_r becomes unity for an infinitely dilute solution it is more useful to define the specific viscosity, η_{sp}, which is given by

$$\eta_{sp} = (\eta_r - 1) = \frac{(t - t_0)}{t_0} \tag{5}$$

It is possible to represent the variation of specific viscosity with concentration as a power series in concentration such as

$$\frac{\eta_{sp}}{c} = [\eta] + k[\eta]^2 c + \ldots \tag{5}$$

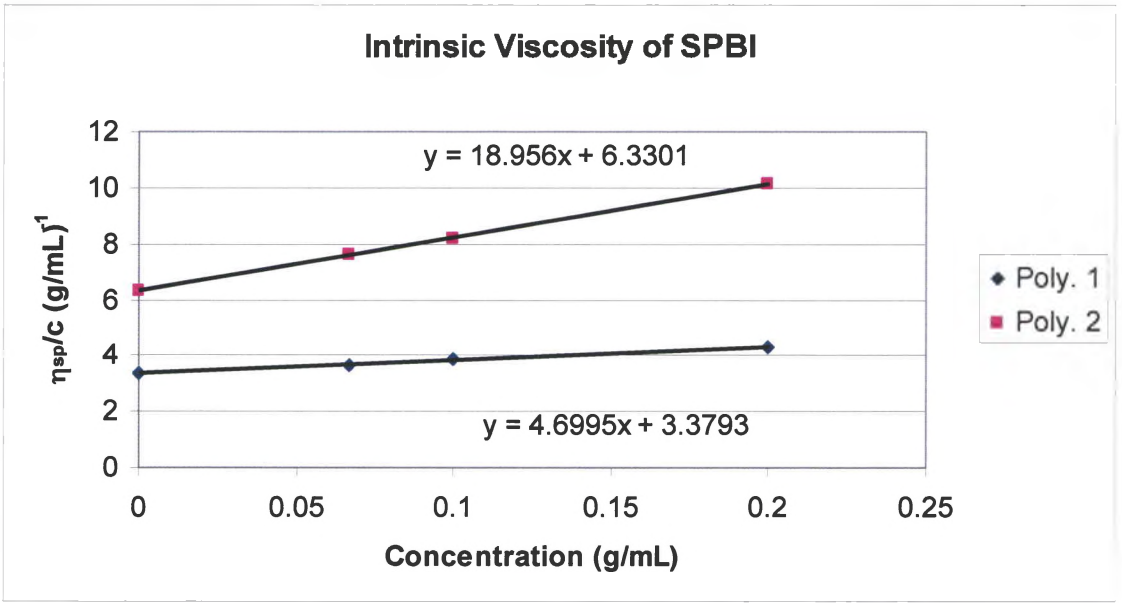
where k is a constant.[24]

The limiting viscosity number (or intrinsic viscosity), $[\eta]$, describes the ability of the polymer molecules to increase the viscosity of the solvent in the absence of any intermolecular interactions. The second term represents the interactions between different molecules in the solution. Measurements of (η_{sp}/c) are normally made of a series of solutions of different concentrations by determining flow times. A typical plot of (η_{sp}/c) vs. c is made for dilute polymer solutions.[24] η_{sp} depends on the polymer concentration, so to extract the "intrinsic" properties of the polymer chain itself, one must extrapolate to zero concentration.[25]

In our experiment, methanesulfonic acid was used as the solvent and three different concentrations were made: 0.20, 0.10, and 0.067 (g/mL). Three trials were made for each concentration and the times were averaged. Then a plot of (η_{sp}/c) vs. c was made and can be seen in Figure 9. The intrinsic viscosity of polymerization 1 was 3.34 $(g/mL)^{-1}$ and 6.33 $(g/mL)^{-1}$ for polymerization 2.

Figure 9

Intrinsic viscosity of SPBI from Polymerization 1 & 2



The units of $[\eta]$ are inverse concentration and the most commonly used concentration is g/dL (grams per 100 mL) so $[\eta]$ is usually expressed as dL/g. Our concentration is measured in g/mL because rigid-rod polymers have a much higher

viscosity than the freely-jointed polymers, which usually use g/dL. As suggested by the units, $[\eta]$ represents essentially the volume occupied by a polymer per unit mass:

$$[\eta] \propto \frac{R^3}{M} \tag{6}$$

where M is the polymer molecular weight. Thus, $[\eta]^{-1}$ is approximately the concentration within the polymer, or the "overlap concentration". More importantly for our purposes is the scaling relationship between $[\eta]$ and molecular weight. This is often called the Mark-Houwink equation:

$$[\eta] = KM^a \tag{7}$$

K and a are constants, which are characteristic for a given polymer-solvent system.[24]

Film Casting

In order to produce cast films, it was necessary to prepare solutions of PANI and SPBI in solvents amenable to standard film casting techniques. Rigid-rod polymers are ordinarily soluble only in strong acids, such as methanesulfonic acid and are not readily amenable to film casting.[26] However, earlier studies have demonstrated that SPBI can be more conveniently solubilized as its triethylammonium (Et_3N^+H) salt in selected organic solvents.[16] In this study, it was solubilized as its Et_3N^+H salt in N-methyl-2-pyrrolidinone (NMP) or methanol. Next, a solution of PANI in NMP was prepared and added to the SPBI/PANI solution. The resultant homogeneous solution was heated to 60 - 80 °C to drive off Et_3N/methanol and trigger the PANI/SPBI acid/base interaction. Isotropic films were then cast from this solution of the PANI/SPBI blend using standard casting techniques.[16] The cast film did not achieve the desired properties, so another method was developed.

A separate attempt to cast films was done without the use of triethylamine. The purpose of this experiment was to protonate the SBPI without converting it to its triethylammonium salt. A mixture of PANI/SPBI in NMP was prepared and sonicated. The sonicator was used because it provides better mixing of the two polymers compared to stirring. Several runs were performed and they were all unsuccessful because SBPI was insoluble in the solution.

In conclusion, it was found that, in general, exposure of the polymerization mixtures to higher reaction temperatures led to samples with reduced solubility, at least partially attributable to certain degree of loss of sulfonic acid functional groups at the employed temperature conditions. It became obvious that the production of a polymer with satisfactory chain length, which is promoted by elevated temperatures, is incompatible with the retention of sulfonic acid functional groups and thereby with solubility. Therefore, modified acidic group-containing monomers, less prone to undergo de-functionalization upon temperature increase, were designed and prepared.

Part III: Preparation of 2-phosphonoterephthalic acid

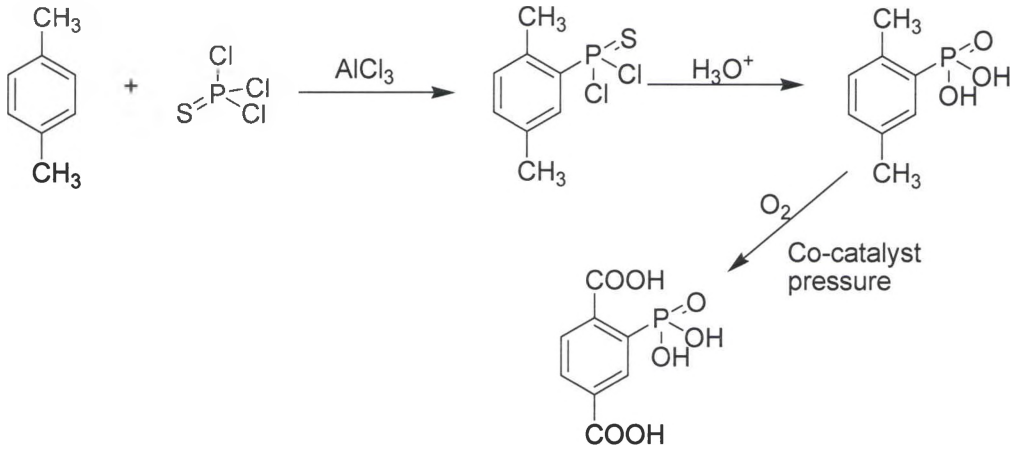
Preparation of 2-phosphonoterephthalic acid

In previously published patent literature the preparation of 2-phosphonoterephthalic acid (**13**) is described, following two different methods. Method 1 relies on the introduction of a phosphorus-containing moiety into the aromatic ring *via* aromatic electrophilic substitution process involving *p*-xylene and thiophosphoryl trichloride, followed by acid hydrolysis of the resultant 2,5-dimethylbenzenephosphonothioic dichloride and a high-pressure Co-catalyzed oxidation in an autoclave of 2,5-dimethylphosphonic acid (Scheme 8).[18] Such method is inherently

complicated and difficult to apply in laboratory conditions, due to the character of the necessary equipment.

Scheme 8

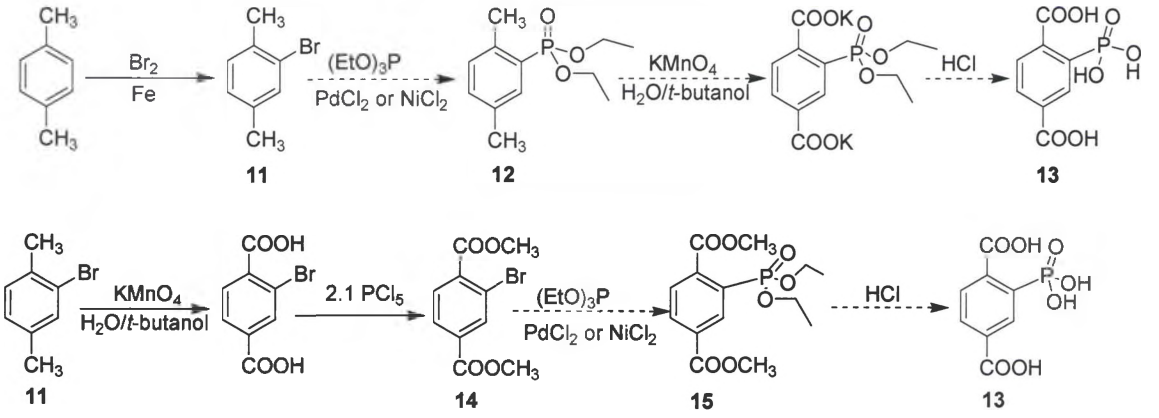
Patent procedure for preparation of 2-phosphonoterephthalic acid from *p*-xylene



Method 2 employs palladium- or nickel-catalyzed coupling of dimethyl 2-bromoterephthalate or 2-bromo-*p*-xylene and triethyl phosphite, followed by acid hydrolysis (Scheme 9).[17] Our repeated attempts to reproduce the latter chemistry led invariably to full recovery of the starting material.

Scheme 9

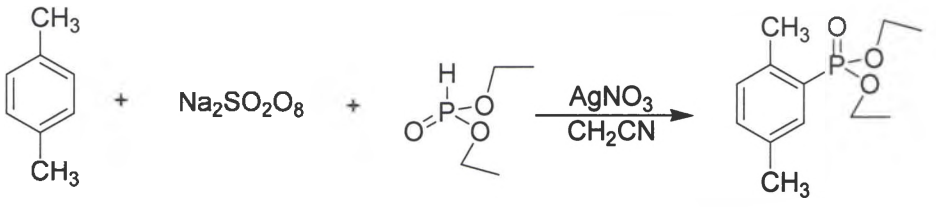
Patent procedure for preparation of 2-phosphonoterephthalic acid *via* Pd- or Ni- catalyzed coupling



Another approach to the introduction of P-containing functionality relies on oxidative coupling of an arene and trialkyl phosphate. This experiment relies on the interaction of an aromatic ring with a triethylphosphite/sodium peroxodisulfate/silver nitrate system (Scheme 10). The silver ions have a high potential for oxidation and so they cause the triethylphosphite to form a radical cation. This radical cation then attacks the aromatic substrate (*p*-xylene), forming an intermediate and thence the arylphosphonate. [27] The product mixture from this experiment did contain some diethyl 2,5-dimethylphenylphosphonate, as well as the starting material (64% total yield). Further research would lead to improvement and optimization of this procedure.

Scheme 10

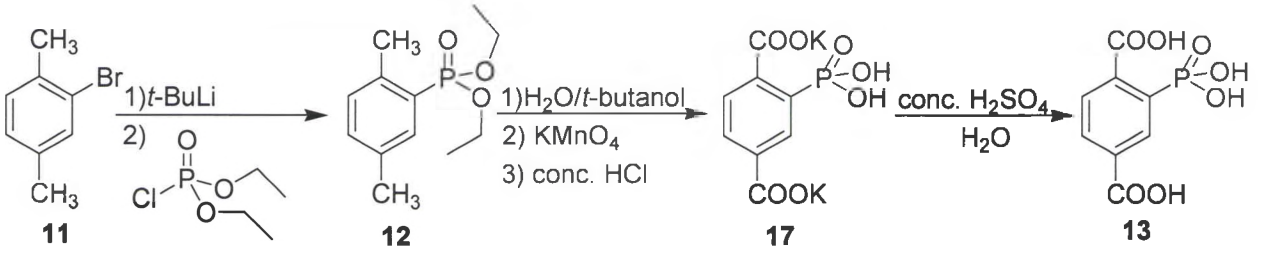
Literature procedure for preparation of diethyl-2,5-dimethylphenylphosphonate



Due to irreproducibility or inconvenience of the cited literature procedures, we developed a new synthetic sequence (Scheme 11). It relies on halogen – lithium exchange, followed by introduction of the phosphorus-containing functionality. 2-Bromo-*p*-xylene[28] is treated with *t*-BuLi at –78 °C and the resultant lithio-derivative is reacted with diethyl chlorophosphosphate to form diethyl 2,5-dimethylphenylphosphonate (**12**). Compound **12**, upon oxidation with $KMnO_4$ yields the dipotassium salt of 2-(diethylphosphonyl)terephthalic acid (**17**). Salt **17** is treated successively with conc. HCl and conc. H_2SO_4 to yield the target compound **13**.

Scheme 11

Synthesis of 2-phosphonoterephthalic acid



Part IV: Preparation of 2-(sulfomethyl)terephthalic acid

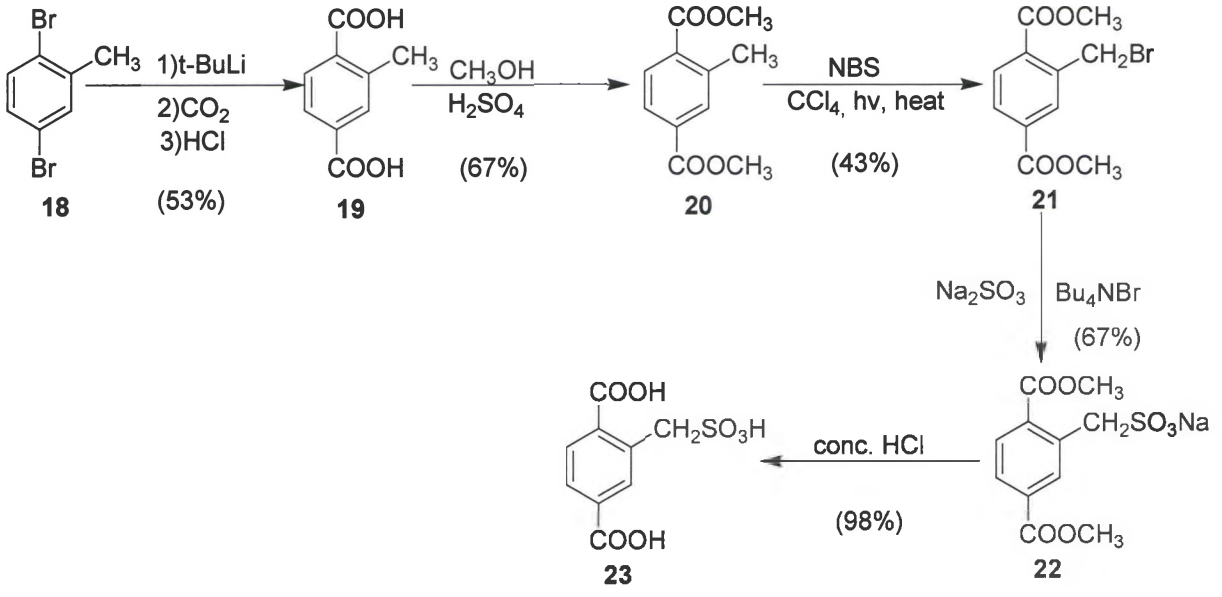
Preparation of 2-(sulfomethyl)terephthalic acid

2-(Sulfomethyl)terephthalic acid is another potentially improved monomer, which can retain its acid functionality during polymerization. By placing a methylene group between the benzene ring and the SO_3H group, the compound will be expected to resist de-sulfonation. 2-(Sulfomethyl)terephthalic acid is a new compound and there are synthetic challenges in making it. The compound has three C-centers connected to a benzene ring. Two of those are in the form of carboxylic acid carbons, while the third is in a lower oxidation state.

The synthesis of 2-(sulfomethyl)terephthalic acid is shown in Scheme 12. The preparation begins with the dilithiation of 2,5-dibromotoluene with *t*-BuLi at –78 °C, followed by reaction with dry ice and subsequent acidification, leading to the introduction of the two carboxyl groups.[29] The resultant 2-methylterephthalic acid (**19**) is esterified[30], then side-chain brominated with NBS, to produce dimethyl 2-(bromomethyl) terephthalate (**21**).[30,31] Compound (**21**) is then subjected to treatment with aqueous Na_2SO_3, in the presence of Bu_4NBr as a catalyst, in a process of nulceophilic replacement of bromine by a sulfonate anion.[32] The resultant sodium salt **22** is treated with conc. HCl to yield the target acid **23**.

Scheme 12

Synthesis of 2-(sulfomethyl)terephthalic acid



CHAPTER 3

EXPERIMENTAL SECTON

General

All chemicals and solvents were of reagent grade purity and used without further purification. Whatman glass backed UV indicator-impregnated 0.25 μ analytical TLC plates were used exclusively. NMR measurements were carried out on a JEOL-FX270 instrument operating at 269.65 MHz for ^{1}H or on a Bruker AVANCE 300 instrument functioning at 300.13 MHz. Frequencies are reported in parts per million (ppm) downfield from the internal reference standard tetramethylsilane. Coupling constants (J) are given in Hertz. High-resolution mass spectra were acquired form Ohio State University using the Q-TOF Electrospray method. Chemical nomenclatures were determined with ACD Labs Chem Sketch nomenclature software.

Synthetic Procedures and Spectroscopic Data

2,5-Dimethylbenzenesulphonic acid (4). *p*-Xylene (10.40 g, 0.08519 mol, 12.00 mL) and concentrated sulfuric acid (20 mL) were added to 125 mL Erlenmeyer flask. The mixture was stirred at 100 °C for 15 minutes.

The mixture was poured into 10 mL of water and then cooled to 0 - 5 °C. The white solid was vacuum filtered and recrystallized from water (10 mL) to yield 28.80 g

(95%) of white solid. Mp 68 - 70 °C. ^{1}H NMR (D_2O) δ 1.63 (s, 3H), 1.94 (s, 3H), 6.51 (m, 2H), 7.07 (s, 1H).

Potassium 2,5-dicarboxybenzenesulfonate (5). 2,5-Dimethlybenzenesulfonic acid (27.00 g, 0.1450 mol) was dissolved in water (200 mL) and the solution was heated to 90 °C. $KMnO_4$ (94.23 g, 0.5963 mol) was added over a period of 2 hours. Water (100 mL) was added to the mixture and it was stirred for 12 hours at 90 °C. The mixture was then cooled, vacuum filtered and concentrated to one-third of its original volume. Concentrated hydrochloric acid was added until acidic reaction occurred, leading to the formation of white precipitate, which was filtered, recrystallized from water (150 mL), vacuum filtered and then washed with small amount of cold water to yield 10.58 g (26 %) of white solid, Mp 375 - 377 °C. Second recrystallization changed the Mp to 377 - 378 °C. Finally **5** was dried under vacuum for 24 hours to yield 9.67 g (23 %) of white solid. Mp 376 – 377 °C. ^{1}H NMR (DMSO-d_6) δ 7.63 (d, J = 7.91 Hz, 1H), 7.98 (dd, J_1 = 7.9 Hz, J_2 = 1.8 Hz, 1H), 8.36 (s, 1H); ^{1}H NMR (D_2O) δ 7.62 (d, J = 8.4 Hz, 1H), 8.14 (dd, J_1 = 7.9 Hz, J_2 = 1.8 Hz, 1H), 8.42 (d, J = 1.3 Hz, 1H).

2-Sulfoterephthalic acid (3) Method A. The K-salt (**5**) was dispersed in conc. H_2SO_4 (50 mL). The mixture was heated and stirred until the salt had dissolved. It was then poured immediately into 50 mL water. Precipitation formed upon cooling, which was vacuum filtered on a fritted funnel and the solid subjected to two more treatments with H_2SO_4. The solid was then dispersed in 30 mL ether, stirred for 5 - 10 minutes, and vacuum filtered. It was then recrystallized from HCl, vacuum filtered, washed with cold

ether and dried at 110°C to give 2.01g (24%) of white solid. Mp 246 - 248 °C. ^{1}H NMR (DMSO-d_6) δ 7.67 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 8.33 (s, 1H), 10.12 (bs, 3H).

Method B (3). Finely ground sodium 2,5-dicarboxybenzenesulfonate (5.00g, 0.01864 mol) and PCl_5 (12.81g, 0.06150 mol) were mixed and heated for three hours at 130 °C. The byproduct, $POCl_3$, was removed under reduced pressure, ether (10 mL) was added and the mixture was gravity filtered. The filtrate was evaporated to yield an oily residue.

Water (20 mL) was added to the residue and the mixture was stirred for 12 hours at 65 °C, followed by reflux for 0.5 hours. Some activated charcoal was added in the last five minutes. The mixture was vacuum filtered and the filtrate was evaporated to dryness under reduced pressure. A white solid was collected weighing 5.07 g (83%). The product was subjected to extensive drying at toluene reflux temperature. Mp 217 – 219 °C. ^{1}H NMR (DMSO-d_6) δ 7.67 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 8.33 (s, 1H), 10.12 (bs, 3H).

4,6-Dinitrobenzene-1,3-diamine (8). 1,5-Dichloro-2,4-dinitrobenzene (24.00 g, 0.10127 mol) was dissolved in ethylene glycol (160 mL) and the mixture heated at 140 °C with stirring. NH_3 gas was passed through the mixture and after ~ 2 hours, precipitate began to form. After ~ 3 - 4 hours the mixture was removed from the heat and vacuum filtered immediately. It was then washed with 400 mL boiling water followed by 400 mL boiling ethanol. The mother liquor was cooled, vacuum filtered and washed with 200 mL

boiling water followed by 200 mL boiling ethanol. After drying the weight of product was 16.01 g (80%).

4,6-Dinitrobenzene-1,3-diamine was recrystallized by dispersing it in 35 mL of DMF and heated until dissolution. Mechanical impurities were removed by hot gravity filtration. The solution was cooled, vacuum filtered, and the solid was washed with ethanol and dried to yield 13.49g (67 %). Mp 308 – 310 °C.

After one more, analogous recrystallization, the product weighed 8.79 g (44%). Mp 308 – 309 °C. The product was then finally recrystallized by dispersing it in 350 mL of 1,4-dioaxane and heated to reflux. Once the mixture was boiling, 55 mL of DMF was slowly added. When the entire product was dissolved, it was allowed to stand for 12 hours. The precipitation was filtered and dried to yield 9.32 g (60 %) of the product as a yellow solid. Mp 312 - 313 °C. ^{1}H NMR (DMSO-d_6) δ 6.12 (s, 1H), 7.63 (s, 4H), 8.83 (s, 1H).

1,2,4,5-Tetraaminobenzene (10). Compound **7** (1.00 g, 0.00505 mol) was dispersed in ethanol (25 mL) and concentrated hydrochloric acid (25 mL) and heated to 125 °C upon stirring. Tin (II) chloride dihydrate (7.00 g, 0.03102 mol) was then slowly added. The solution was refluxed for four hours and then vacuum filtered. The solid was washed with a small amount of methanol, followed by ether and dried to yield 1.10 g (77%) of white solid. ^{1}H NMR (DMSO-d_6) δ 6.85 (s, 2H), 7.30 (bs, 8H).

The product was recrystallized by dispersing it in concentrated hydrochloric acid and heated to reflux. Water was then added in small portions to full dissolution. Then activated charcoal was added and the mixture was stirred and heated for 5 minutes.

Finally the mixture was hot filtered through celite and cooled at ambient temperature for 24 hours in a sealed container. The product was filtered in a vacuum pistol with a fritted funnel and washed with large quantities of HCl, THF, and ether under N_2-pressure. Then the product was placed into a vacuum desiccator, and dried for 12 hours.

Polyphosphoric acid. Conc. H_3PO_4 (100.0 g, 1.02 mol) was placed in an ice bath, under nitrogen, while P_2O_5 (63.39 g, 0.447 mol) was slowly added. The mixture was left stirring in an ice bath for about 30 minutes. The mixture was kept in a vacuum desiccator.

Polymerization 1. 2-Sulfoterephthalic acid (4.6057 g, 0.0187 mol), 1,2,4,5-tetraaminobenzene tetrahydrochloride (5.1858 g, 0.0375 mol), and 13.46g PPA (77% P_2O_5) were stirred slowly under vacuum (420 mm Hg) at ambient temperature. The vacuum was used to dehydrochlorinate 1,2,4,5-tetraaminobenzene. The mixture was heated to 65 °C over a period of 3 hours and held at that temperature for 16 hours.

The temperature was increased to 75 °C and held there for one hour then raised to 80 °C and held there for three hours. The vacuum was stopped, the flask was removed from heat, and P_2O_5 (11.24 g, 0.0792 mol) was added. Once the addition was complete, the vacuum was turned back on and the temperature was raised to 100 °C over a period of a 0.5 hours. When the desired temperature was reached, the vacuum was turned off and a lead acetate bubbler was turned on. The reaction was held at 100 °C for 16 hours with the bubbler on. The temperature was then raised to 140 °C over a period of eight hours, while all other conditions remained the same and then held at that temperature for 12

hours. Stir opalescence was observed and the polymer was left curing for 72 hours.

The polymer was removed from the flask, placed in DI water (500 mL), and left for 12 hours. The polymer was chopped-up in a blender with the DI water, vacuum filtered on a medium fritted funnel, washed with DI water (500 mL), and added to a Soxhlet extractor with triethylamine (100 mL). The Soxhlet extractor was set at 100 °C and the mixture was left for 60 hours. The polymer was placed back in the blender with DI water and some glacial acetic acid, used to neutralize the triethylamine. The polymer was then vacuum filtered again, washed with water, placed in the Soxhlet extractor, and held at 100 °C for 48 hours.

The polymer was then vacuum filtered on a medium fritted funnel and washed successively with methanol (200 mL), THF (200 mL), and benzene (200 mL). The sample was divided into four parts and two were freeze-dried at –5 °C and the other two were freeze-dried at –20 °C. The samples were left freeze-drying for 72 hours. Then the samples were placed in a drying pistol with P_2O_5 and dried at acetone reflux temperature for 72 hours. The P_2O_5 was replaced and the polymer was dried for 60 hours at *n*-butyl alcohol reflux temperature.

Polymerization 2. A mixture of 2-sulfoterephthalic acid (4.7054 g, 0.0191 mol), 1,2,4,5-tertaaminobenzene tetrahydrochloride (5.0616g, 0.0366 mol), and 13.1597g PPA (77% P_2O_5) was stirred under vacuum (650 mm Hg) at ambient temperature. The mixture was heated to 65 °C over a period of 3 hours and held at that temperature for 12 hours. The temperature was increased to 80 °C and left for 4 hours. The mixture was then cooled to room temperature, the vacuum turned off, and P_2O_5 (11.18 g, 0.0788 mol)

added. Then the vacuum was turned back on, the temperature was raised to 60 °C over a period of 2 hours, the vacuum was turned off, a lead acetate bubbler was turned on, and temperature was raised to 100 °C and left for 12 hours. The mixture was then heated to 155 °C and left for 12 hours. Stir opalescence was seen after 12 hours, temperature was held at 155 °C for 72 more hours, and then the polymerization was stopped.

The polymer was removed from the flask, placed in DI water (500 mL), and left for 12 hours. The polymer was chopped-up in a blender with the DI water, vacuum filtered on a medium fritted funnel, washed with DI water (500 mL), and placed in a Soxhlet extractor with DI water for 192 hours. The Soxhlet extractor was set at 100 °C. Then the polymer was vacuum filtered on a fritted funnel and washed with methanol (300 mL). The sample was divided into four parts and two were freeze dried at –5 °C and the other two were freeze dried at –20 °C. The samples were left freeze-drying for 72 hours. Then the samples were placed in a vacuum pistol with P_2O_5 and dried at *n*-butyl alcohol reflux temperature for 120 hours.

Viscosity measurements. 99.5% methanesulfonic acid (30 mL) was filtered, to remove any dust or particles in the solution. 20 mL of acid was pipetted into the flask with SPBI (0.0402 g, 0.000128 mol) and stirred for 48 hours. The viscosity measurements were conducted with a Cannon 150 (D795) Ubbelohde, using methanesulfonic acid as the solvent. Two separate viscosity tests were done, one for each polymerization. The water bath was at 29.60^{0}C for the first measurement (polymerization 1 sample) and 29.97^{0}C for the second measurement (polymerization 2 sample). First the solvent was run alone and three time trials were taken. Then three

different concentration trials were done: 0.20 g/mL, 0.10 g/mL, and 0.06667 g/mL. Three time trials were done at each concentration.

Attempted film casting experiment 1. A mixture of PANI (0.0180 g, 0.0000497 mol) and NMP (3.084 g, 0.311mol) was stirred at room temperature for 72 hours. At the same time, a mixture of SPBI (0.0313 g, 0.0000999 mol), triethylamine (0.0928 g, 0.000919 mol)), and NMP (3.084 g, 0.0311 mol) was stirred at room temperature also for 72 hours. The PANI solution was transferred into the flask containing SPBI and the mixture was stirred for thirty minutes at 100 °C to remove triethylamine.

The solution was transferred into a casting dish and placed into a vacuum/drying pistol with P_2O_5, leveled the dish, and dried at acetone reflux temperature (1mm Hg) for 12 hours. The film was cooled to room temperature with the vacuum turned off, floated the film off the dish with water, placed between two pieces of Teflon, and dried again at *n*-butyl alcohol reflux temperature for 12 hours. The vacuum and heat were turned off and the film was cooled to ambient temperature. The film began to fall apart after 7 days, which was indicative of poor quality.

Attempted film casting experiment 2. A mixture of PANI (0.0150 g, 0.0000414 mol), SPBI (0.0260 g, 0.0000830 mol, first or second polymerization sample), and NMP (5.14 g, 0.0519 mol) was sonicated at ambient temperature for 48 hours. SPBI was insoluble in the solution, making blending impossible in these conditions.

Attempted film casting experiment 3. A mixture of SPBI (0.0331 g,

0.000106 mol, first or second polymerization sample), triethylamine (0.0928 g, 0.000919 mol), and NMP (4.112 g, 0.0415 mol) was sonicated at ambient temperature for 72 hours. Then added PANI (0.0180 g, 0.0000497 mol) in NMP (1.028 g, 0.0104 mol) to the SPBI mixture and left for 12 hours. Vacuum filtered the mixture and discovered that the SPBI had not dissolved.

Attempted film casting experiment 4. A mixture of SPBI (0.0335 g, 0.000107 mol, first or second polymerization sample), methanol (8.85 g, 0.276 mol, 7 mL), and triethylamine (0.0928 g, 0.000919 mol) was sonicated at ambient temperature for 72 hours. Methanol (3.16 g, 0.0988 mol, 4 mL) was added to the mixture because some methanol had evaporated. Then PANI (0.0185 g, 0.0000510 mol) in NMP (4,112 g, 0.0415 mol) was added to the SPBI and heated at 80 °C for 12 hours with a distillation flask to remove methanol. Additional NMP (1.028 g, 0.0104 mol) was added to the mixture and a drying tube was put in place of the distillation flask. The mixture was heated again at 80 °C for 72 hours. SPBI was insoluble in the solution even after 72 hours of heating.

Attempted film casting experiment 5. A mixture of SPBI (0.0186 g, 0.0000594 mol, first or second polymerization sample), PANI (0.0186 g, 0.0000513 mol), and NMP (6.168 g, 0.0622 mol, 6 mL) was sonicated for 12 hours at ambient temperature. Triethylamine (0.928 g, 0.000919 mol) was added to the flask and sonicated for 72 hours. Vacuum filtered the mixture and discovered SPBI had not dissolved.

2-Bromo-*p*-xylene (10). Iron powder (0.64 g, 0.01146 mol) and *p*-xylene (37.376 g, 0.3520 mol) were stirred at room temperature while bromine (1.0 mL, 3.12 g, 0.0390 mol) was added drop wise. Once the reaction began (evolution of gas), bromine (15.0 mL, 46.8 g, 0.586 mol) was added drop-wise over 2 hours, while the temperature was controlled by a water bath. After addition was complete, the water was removed and the solution was stirred for an additional two hours at ambient temperature. The solution was vacuum filtered, to remove any unreacted iron and washed successively with aqueous Na_2SO_3 (50 mL), dilute aqueous NaOH (50 mL), and water (2 x 25 mL). The organic layer was dried ($MgSO_4$) and filtered to yield 43.3g (67%) of product. The product was further purified by vacuum distillation and collecting the fraction at 115 °C (1 mm Hg), giving 28.65g (44%) of pure product. ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H), 2.34 (s, 3H), 6.99 (d, J = 7.7 Hz, 1H), 7.09 (d, J = 7.7 Hz, 1H), 7.35 (s, 1H).

Attempted preparation of diethyl 2,5-dimethylphenylphosphonate (12). A mixture of $PdCl_2$ (0.33 g, 0.0019 mol) or equimolar amount of $NiCl_2$, 2-bromo-*p*-xylene (3.50 g, 0.0189 mol), and triethyl phosphite (13 mL, 0.0756 mol) was stirred at 150 °C for 12 hours. The solution was cooled to room temperate and partitioned between 1,2-dichloroethane (15 mL) and water (15 mL). The organic layer was washed with water (2 x 15 mL), dried ($MgSO_4$) and vacuum distilled. Fractions were collected at 35 °C and 115 °C. NMR showed the distilate to be a combination of 2-bromo-*p*-xylene and triethyl phosphite.

2-Bromoterephthalic acid. A mixture of 2-bromo-*p*-xylene (15.00 g,

0.0811mol), H_2O (200 mL), and *t*-butanol (200 mL) was heated to 110 ^{0}C. $KMnO_4$ (52.6 g, 0.333 mol) was slowly added and the mixture left refluxing for 12 hours. The mixture was cooled to ambient temperature and vacuum filtered on a fritted funnel. The filtrate was concentrated to half of its original volume, cooled with an ice bath, and acidified with conc. HCl. A white precipitate was separated, vacuum filtered, and washed with cold water. The solid was air-dried to yield 0.37 g (52%). ^{1}H NMR (DMSO-d_6) δ 7.80 (d, J = 7.9 Hz, 1H), 7.96 (dd, J_1 = 7.9, J_2 = 1.8 Hz, 1H), 8.12 (d, J = 1.8, 1H).

Dimethyl 2-bromoterephthalate (14). A mixture of 2-bromoterephthalic acid (10.20 g, 0.042 mol) and PCl_5 (18.20 g, 0.0874 mol) was heated at 160 °C for three hours. By-product ($POCl_3$) was removed under reduced pressure and ether (10 mL) was added to the residue. The solution was gravity filtered and the solvent was removed. Methanol (75 mL) was added at 0 °C and the solution was stirred at reflux for 12 hours. The solvent was removed and the reside was passed through a short silica gel column. The column was successively eluted with hexane/methylene chloride (hexane: CH_2Cl_2 = 3:1, 200 mL) then with hexane/methylene chloride (hexane: CH_2Cl_2 = 1:1, 200 mL) and then with pure methylene chloride. The CH_2Cl_2 fraction was collected and the solvent removed to yield 5.89g (52%) of solid. Mp 63 – 64 °C. ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 1H), 3.42 (s, 1H), 7.36 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 8.25 (s, 1H).

Attempted preparation of dimethyl 2-(diethoxyphosphoryl)terephthalate (15). A mixture of dimethyl 2-bromoterephthalate (5.16 g, 0.0189 mol), triethyl

phosphite (12.56 g, 0.0756 mol), and palladium chloride (0.34 g, 0.0019 mol) was heated to 150 °C under nitrogen for three hours and then cooled to room temperature. The solution was then partitioned with water (15 mL), 1,2-dichloroethane (EDC) (15 mL) and washed with water (2 x 15 mL). The EDC layer was dried ($MgSO_4$), filtered, and vacuum distilled. Residue was passed through a short silica gel column and the column was successively eluted with hexane/CH_2Cl_2 (hexane: CH_2Cl_2 = 1:1, 400 mL) and pure CH_2Cl_2. The CH_2Cl_2 fraction was collected and the solvent removed. NMR revealed that the residual was the starting material.

Diethyl 2,5-dimethylphenylphosphonate (12). *p*-Xylene (3.06 g, 0.0300 mol) and $HPO_3C_2H_5$ (20.72 g, 0.150 mol) in CH_3CN (30 mL) were added to $Na_2S_2O_8$ (14.29 g, 0.060 mol) in H_2O (150 mL) and stirred under nitrogen for 10 minutes. $AgNO_3$ (1.02 g, 0.0060 mol) in H_2O (30 mL) was added to the mixture and left under nitrogen for 48 hours at room temperature. The solution was extracted with CH_2Cl_2 (25 mL) and dilute aqueous sodium carbonate (25 mL). The organic layer was dried ($MgSO_4$), filtered, and solvents removed to yield 4.49 g (64%) yellow liquid. NMR showed a mixture of the starting material and the product.

Diethyl 2,5-dimethylphenylphosphonate (12). The glassware was dried in an oven and assembled hot. The system was evacuated and put under nitrogen. A mixture of anhydrous THF (10 mL) and 2-bromo-*p*-xylene (2.00 g, 0.0108 mol) was stirred at –20 °C while *t*-butyllithium (6.36 mL, 0.0108 mol, 1.7 M pentane solution) was slowly added. The reaction mixture was left stirring for 1 hour and then warmed to –10 °C within 30

minutes. A solution of diethylchlorophosphate (1.86 g, 0.0108 mol) in anhydrous THF (5 mL) was stirred under nitrogen at 0 °C while the 2-bromo-*p*-xylene solution was slowly added. Stirring was continued for 12 hours at ambient temperature. The reaction mixture was washed successively with aqueous ammonium chloride (2.00 g NH_4Cl in 50 mL water) and ether (15 mL). The organic layer was dried ($MgSO_4$), filtered and solvents removed. Residual was passed through a short silica gel column. The column was eluted with pure hexane (200 mL) and hexane/ethyl acetate (hexane: ethyl acetate = 1:1, 400 mL). The hexane/ethyl acetate fraction was collected and solvents evaporated to yield 2.05 g (78%) clear pale yellow product. ^1H NMR ($CDCl_3$) δ 1.33 (t, J =7.5 Hz, 6H), 2.34 (s, 3H), 2.52 (s, 3H), 4.04-4.19 (m, 4H), 7.15 (d, J = 5.8 Hz, 1H), 7.22 (d, J = 13.5 Hz, 1H), 7.70 (d, J = 14.7 Hz, 1 H).

2-Phosphonoterephthalic acid (13). A mixture of diethyl 2,5-dimethylphenylphosphonate (2.19 g, 0.00904 mol), water (30 mL) and *t*-butanol (30 mL) was stirred at 110 °C while potassium permanganate (5.71 g, 0.0362 mol) was slowly added. The mixture was left refluxing for 2 hours. Temperature was reduced to 80 °C and stirring continued for 12 hours. The mixture was cooled to ambient temperature, vacuum filtered, concentrated to 1/3 of its original volume, and acidified with conc. HCl until acidic reaction occurred leading to the formation of a white precipitate. The mixture was left for 12 hours at –10 °C. The water was evaporated and CH_2Cl_2 (10 mL) was added to the solid. The solution was vacuum filtered and washed with ether (10 mL) to yield 1.93 g (56%) white paste.

Potassium 2-phosphonoterephthalate was placed into a flask with concentrated

sulfuric acid (20 mL) and water (10 mL). The flask was cooled for 12 hours in a 4 °C refrigerator. Vacuum filtered on a fritted funnel and washed with cold ether (5 mL) to yield 1.30 g (96%) of white solid. ^{1}H NMR (D_2O) δ 7.87-7.92 (m, 1H), 8.22 (d, J = 6.6 Hz, 1H), 8.50 (d, J = 12.9 Hz, 1H).

2-Methylterephthalic acid (19). The glassware was dried in an oven and assembled hot. The system was evacuated and put under nitrogen. A mixture of anhydrous THF (75 mL), 2,5-dibromotoluene (5.00 g, 0.200 mol), and tetramethylethylenediamine (24 mL) was stirred under nitrogen and then cooled to –20 °C while *t*-BuLi (94.00 mL, 0.160 mol, 1.7 M pentane solution) was slowly added. The reaction was left stirring for 3 hours. At ambient temperature, the reaction mixture was added to an 800 mL beaker filled, half filled with finely ground dry ice and stirred until all the dry ice had dissolved. The reaction mixture was then slowly added to a 5% aqueous NH_4Cl (200 mL), washed with ethyl acetate (25 mL), dried (Na_2SO_4), filtered, and solvents removed. Hexane (5 mL) was added to the flask, heated with a hot gun, and placed in a –27^{0}C freezer for 12 hours. Residual was vacuum filtered and washed with the mother liquor to yield 1.90 g (53%) of tan solid. ^{1}H NMR (methanol-d_4) δ 2.59 (s, 3H), 7.85-7.91 (m, 3H).

Dimethyl 2-methylterephthalate (20). 2-Methylterephthalic acid (1.90 g, 0.0105 mol), concentrated sulfuric acid (0.4 mL), and methanol (10 mL) were combined at 0 °C and then heated to reflux. Once the mixture was refluxing, additional methanol (20 mL) was added and the mixture was left refluxing for 12 hours. The reaction mixture

was poured into water (10 mL) and then the solution was extracted with ether (10 mL). The organic layer was dried ($MgSO_4$) and the solvents were removed. Residual was passed through a short silica gel column and the column was eluted with pure methylene chloride (400 mL), followed by hexane/ethyl acetate (hexane: ethyl acetate = 3:1, 600 mL). The hexane/ethyl acetate fraction was collected and the solvents were removed to yield 1.46 g (67%) of orange liquid. ^{1}H NMR ($CDCl_3$) δ 2.64 (s, 3H), 3.93 (s, 3H), 3.94 (s, 3H), 7.90 - 7.94 (m, 3H).

Dimethyl 2-(bromomethyl)terephthalate (21). A mixture of dimethyl 2-methylterephthalate (0.81 g, 0.0039 mol), CCl_4 (9.20 mL), and NBS (0.82 g, 0.00461 mol) was refluxed with a heat lamp and no stirring for 12 hours. The mixture was vacuum filtered, washed with CCl_4 (2 mL), and solvents removed from filtrate. Then ethanol (2 mL) was added to the residue and placed in –27 °C freezer for 60 hours.

Precipitated solid was vacuum filtered, washed with cold ethanol, and solvents removed from filtrate. Residual was passed through a silica gel column and eluted with hexane/ethyl acetate (hexane: ethyl acetate = 3:1). The solvents were removed to yield 0.28 g (25%) of white paste. ^{1}H NMR ($CDCl_3$) δ 3.96 (s, 3H), 3.98 (s, 3H), 4.97 (s, 2H), 8.02 (s, 1H), 8.13-8.14 (m, 2H).

Sodium 2,5-bis(methoxycarbonyl)phenylmethanesulfonate (22). Dimethyl 2-bromomethylterephthalate (0.28 g, 0.000975 mol) was added to tetrabutylammoniumbromide (0.0079 g, 0.0000246 mol) in water (4 mL). Na_2SO_3 (0.145 g, 0.00115 mol) in ethanol (4 mL) was added to the mixture and it was refluxed for 12

hours. The flask was cooled to room temperature and solvents removed. Then methylene chloride (10 mL) was added and the mixture vacuum filtered and washed with methylene chloride (5 mL) to yield 0.20 g (67%) of white crystals. ^{1}H NMR (D_2O) δ 3.94 (s, 3H), 3.95 (s, 3H), 4.67 (s, 2H), 7.92 (d, J = 8.7 Hz, 1H), 8.04 – 8.07 (m, 2H).

2-(Sulfomethyl)terephthalic acid (23). Sodium 2,5-bis (methoxycarbonyl) phenylmethanesulfonate (0.20 g, 0.00064 mol) was added to conc. HCl (4 mL) and refluxed fro 12 hours. The flask was cooled to room temperature and then placed in a – 27^{0}C freezer for 12 hours. Solid was vacuum filtered and washed with ether to yield 0.17 g (98%) of wet white solid. Dried the solid at 65 °C for 5 hours. Mp 290 – 292 °C. ^{1}H NMR (D_2O) δ 4.70 (s, 2H), 7.93 (d, J = 8.0 Hz, 1H), 8.07 – 8.08 (m, 2H); HRMS (FAB^+) *m/z* Calcd. for $C_9H_8SO_7$ $[M+Na]^+$ 282.9888, found 282.9893.

CHAPTER 4

CONCLUSIONS

The objective of this research effort was the novel synthesis and processing of rigid-rod polymers that are sufficiently compatible to be homogeneously dispersed on the molecular scale, leading to a angstrom-scale composite (ÅSC). Any investigation into the synthesis and processing of rigid-rod polymers is dependent upon first understanding the preparation of the monomers present in the polymer of interest. The production of SBPI has been investigated and recorded in the literature. However, the reproducibility has not been demonstrated.

Through analysis of SPBI, the effect of its monomers on the resultant polymer was determined. The analysis showed that when samples are cured at high temperatures the resultant polymer structure loses acid functional groups. However, if samples are cured at low temperatures the resultant polymer structure has a low molecular weight and intrinsic viscosity.

These results suggest that a new acidic monomer must be used for the production of the rigid-rod polymer or the resultant polymer will not be produced with consistent results. In addition, the procedure for 1,2,4,5-tetraaminobenzene was changed to improve its yield and environmental conditions.

Two different compounds were synthesized, which could replace 2-sulfoterephthalic acid. The first is 2-phosphonoterephthalic acid, a compound that has

been previously reported in recent literature.[17,18] The second is 2-(sulfomethyl)terephthalic acid, which is a new compound. New procedures were developed for both monomers.

This research effort determined the product irregularity of SPBI and developed new monomers to be used in the preparation of SPBI. The information can be used for the production of other rigid-rod polymers and for the production of ÅSC.

FUTURE RESEARCH

Future research calls for the polymerization of 2-phosphonoterephthalic acid or 2-(sulfomethyl)terephthalic with 1,2,4,5-tetraaminobenzene to form PPBI and SMPBI. Then PPBI and SMPBI can be blended with PANI to form the ÅSC. The two reaction schemes are shown in Figures 10 and 11.

Figure 10

Preparation of PPBI and SMPBI

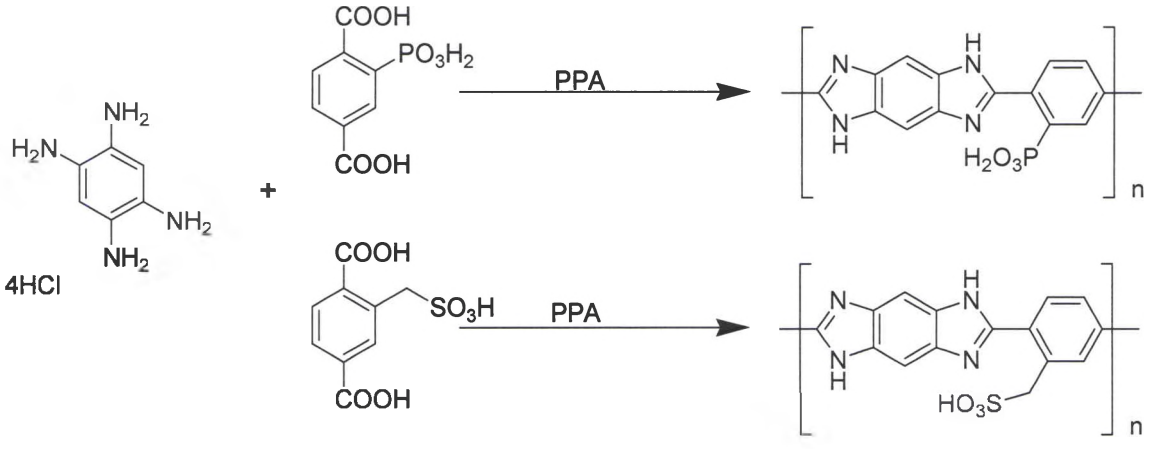
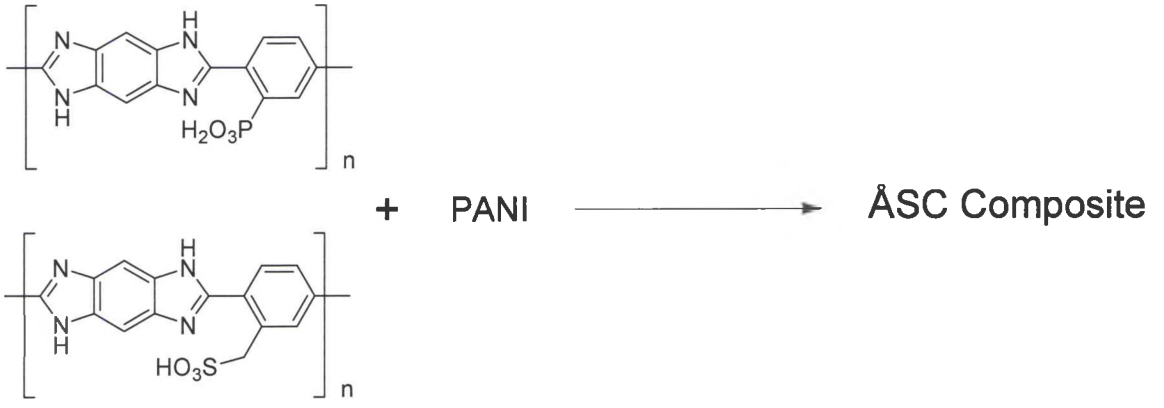


Figure 11

Preparation of two new ÅSCs



In addition, more research can be done to develop a better procedure for making large quantities of 2-phosphonoterephthalic acid and 2-(sulfomethyl)terephthalic acid.

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